(51) International Patent Classification⁷: **C01B 3/08,**
6/04, 6/24, B01J 7/00

(21) International Application Number: PCT/US02/00923

(22) International Filing Date: 11 January 2002 (11.01.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
60/261,616   12 January 2001 (12.01.2001)   US
60/261,601   12 January 2001 (12.01.2001)   US
60/261,600   12 January 2001 (12.01.2001)   US

(63) Related by continuation (CON) or continuation-in-part
(CIP) to earlier applications:
US   09/707,105 (CIP)
Filed on   6 November 2000 (06.11.2000)
US   09/309,198 (CIP)
Filed on   10 May 1999 (10.05.1999)

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(81) Designated States (national): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG,
SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ,
VN, YU, ZA, ZM, ZW.

(84) Designated States (regional): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR,
GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent
(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR,
NE, SN, TD, TG).

Published:
—   with international search report
—   before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: STORAGE, GENERATION, AND USE OF HYDROGEN

(57) Abstract: A composition comprising a carrier liquid; a dispersant; and a chemical hydride. The composition can be used in
a hydrogen generator to generate hydrogen for use, e.g., as a fuel. A regenerator recovers elemental metal from byproducts of the
hydrogen generation process.

STORAGE, GENERATION, AND USE OF HYDROGEN

This invention was made with Government support under contracts awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

5 ## BACKGROUND

This invention relates to the storage, generation, and use of hydrogen.

Traditional storage technologies for hydrogen include bottled compressed hydrogen gas and bottled liquid hydrogen. The use of such technologies has been limited because of dangers in storage and in handling and transporting. Hydrogen gas and cryogenic liquid
10   in storage or transport have evidenced instability and high combustibility.

Hydrogen also has been incorporated into metal hydrides from which the hydrogen can be released by the application of water. U.S. Patent No. 4,155,712, issued May 22, 1979, to Walter G. Taschek, discloses a hydrogen generator in which water vapor is combined with a metal hydride, preferably calcium hydride (CaH_2) or lithium
15   aluminum hydride ($LiAlH_4$) to release hydrogen (H_2) stored in the hydride. U.S. Patent No. 4,261,955, issued April 14, 1981, to Cornelius E. Bailey, Jr., et al, describes subjecting a metal hydride, such as calcium hydride, to water vapor to generate essentially pure hydrogen.

Known hydrogen-fueled power devices include fuel cells, internal combustion engines,
20   and other devices.

Mixing a light metal hydride, such as lithium hydride and a reactant, such as water to produce hydrogen also produces, as a byproduct, a hydroxide of the elemental metal, lithium hydroxide. Although the generation of hydrogen in such a process can occur on a continuing basis, the byproduct, i.e., the lithium hydroxide, accumulates until
25   removed.

SUMMARY

In general, in one aspect, the invention features a composition comprising a carrier liquid; a dispersant; and a chemical hydride.

5   Implementations of the invention may include one or more of the following features. The chemical hydride has a concentration of at least 40% by weight of the composition. In some examples, the chemical hydride has a concentration of less than 75% by weight of the composition, for example, about 61%. In other examples, the chemical hydride has a concentration of more than 90%. The carrier liquid includes an organic liquid.

10   The organic liquid includes mineral oil, e.g., a light mineral oil. The carrier liquid includes a hydrocarbon. The hydrocarbon includes an alkane. The alkane is selected from a group consisting of pentane and hexane. The composition is in the form of a slurry. The carrier liquid has a viscosity in the range of about 32 Saybolt Universal seconds (S.U.s.) at standard temperature and pressure (STP) to about 100 S.U.s but

15   preferably about 42 S.U.s. to about 59 S.U.s. The carrier liquid exhibits a flash point in the range of about 100 °C to about 350 °C and preferably about 154 °C to about 177 °C.

The chemical hydride includes a light metal hydride. The light metal hydride is selected from the group consisting of lithium hydride, lithium borohydride, lithium aluminum

20   hydride, sodium hydride, sodium borohydride, sodium aluminum hydride, magnesium hydride, and calcium hydride. The chemical hydride includes lithium hydride.

The dispersant comprises a triglyceride. The triglyceride includes a triglyceride of oleic acid. The triglyceride includes triolein. The chemical hydride includes magnesium hydride.

25   In general, in another aspect, the invention features a method that includes mixing chemical hydride particles and an oil to form a slurry.

In general, in another aspect, the invention includes a composition comprising a mass of chemical hydride particles in a concentration of about 90-95% by weight of the composition, and an oil coating the chemical hydride particles, the oil comprising 5-10% by weight of the composition.

5   In general, in another aspect, the invention features apparatus comprising: a reservoir containing a chemical hydride, and a mechanism configured to introduce a reactant to selected different portions of the chemical hydride to effect hydrogen generating reactions at different locations within the reservoir.

Implementations of the invention may include one or more of the following features.
10   The reservoir includes a canister. The reservoir includes chambers that contain chemical hydride. The mechanism includes conduits that have open delivery ends arranged to introduce the reactant to respective selected portions of the chemical hydride. The conduits are arranged in parallel. The ends are located at different distances along an axis of the reservoir. The mechanism is configured to be movable
15   relative to the chemical hydride contained in the reservoir. The conduits comprise needles. The mechanism includes a valving system that controls the introduction of the reactant to the different portions. The reservoir includes an exit for hydrogen generated in the reaction.

In general, in another aspect, the invention features a hydrogen fuel generation
20   assembly that includes: (a) a reservoir for a slurry comprising a carrier liquid, a triglyceride dispersant, and a chemical hydride; (b) a reservoir for water; (c) a hydride reactor in communication with said slurry reservoir and said water reservoir and adapted to receive the slurry and water from the reservoirs, respectively, and to mix the slurry and water to effect release of hydrogen from the slurry; (d) a tank for receiving
25   the hydrogen from said reactor and for receiving hydroxide byproduct from said reactor, and for facilitating separation of the hydrogen and the hydroxide byproduct; (e) a heat exchanger for receiving the hydrogen from said tank and adapted to condense water from the hydrogen; (f) a gas-liquid separator for receiving hydrogen and water

from said heat exchanger and adapted to separate the water from the hydrogen and to dispense dried hydrogen; (g) a conduit for conveying the water from said separator to said water reservoir; and (h) a conduit for conveying the dried hydrogen to a hydrogen-fueled power-producing device.

5   Implementations of the invention may include one or more of the following features. The reactor includes a tubular housing and a mixer for mixing the slurry and the water. The tank is provided with an outlet for flowing hydrogen gas from the tank, and a bottom portion for the receiving of the hydroxide byproduct. The power-producing device includes a selected one of a fuel cell, an internal combustion engine, and an

10   external combustion engine. There are also conduit means for conveying condensed water from said fuel cell to said water reservoir. The power-producing device includes a selected one of the internal combustion engine and the external combustion engine and the assembly further includes a condenser for condensing water from water vapor from said engine, said condenser being in communication with means for conveying

15   water from said condenser to said water reservoir.

In general, in another aspect, the invention includes a method for generating hydrogen fuel for a power-producing hydrogen-fueled device, the method includes the steps of: (a) providing a slurry comprising an organic carrier liquid, a triglyceride dispersant, and a chemical hydride; (b) mixing said slurry with water to effect release of hydrogen from

20   the slurry; (c) removing water vapor from the hydrogen released from the slurry, to provide dried hydrogen; and (d) conveying the dried hydrogen to the hydrogen-fueled device for the production of power.

Implementations of the invention may include one or more of the following features. The organic carrier liquid includes a light mineral oil. The mixing of said slurry and

25   said water is undertaken with an auger. The water removed from the hydrogen is returned back to a source of the water for mixing with the slurry. Water condensed from a fuel cell is returned to a source of the water for mixing with the slurry.

In general, in another aspect, the invention features a regeneration assembly for

converting metal oxides and hydroxides to elemental metals, the assembly comprising:
(a) a reactor adapted to receive the metal hydroxide and carbon, and adapted to retain a
molten carbon-dissolving metal in the reactor; (b) means for flowing gases comprising
the elemental metal in gaseous form, carbon monoxide, and hydrogen from said
5   reactor; (c) a condenser adapted to receive the gases flowed from said reactor and
adapted to discharge carbon monoxide and hydrogen from a first outlet and the
elemental metal, metal oxide, and carbon from a second outlet; (d) a separator adapted
to receive the elemental metal, oxide thereof, and carbon from said condenser and to
discharge the elemental metal in gaseous form; (e) means for flowing the elemental
10   metal and the carbon dissolving metal in liquid form from said reactor to said separator;
and (f) means for flowing the metal oxide and the carbon dissolving metal from said
separator to said reactor.

Implementations of the invention may include one or more of the following features. A
second separator receives the carbon monoxide and hydrogen from said condenser, said
15   second separator having a first outlet for discharging carbon monoxide and a second
outlet for discharging hydrogen.

In general, in another aspect, the invention features a method for converting metal
oxides and metal hydroxides to elemental metals thereof, the method comprising the
steps of: (a) admitting the metal hydroxide and carbon into a reactor having molten
20   carbon-dissolving metal therein; (b) flowing gases comprising the elemental metal in
gaseous form, carbon monoxide and hydrogen from the reactor to a condenser; (c)
condensing out the elemental metal and oxide thereof, and carbon, and flowing same to
a separator; (d) flowing carbon monoxide and hydrogen from the condenser; (e)
flowing the elemental metal and the carbon dissolving metal from the reactor to the
25   separator; (f) flowing elemental metal oxide and the carbon dissolving metal from the
separator to the reactor; and (g) flowing the elemental metal from the separator. In
some implementations, an inert gas is flowed into the reactor.

Other advantages and features will become apparent from the following description and

from the claims.

DESCRIPTION

(Figures 1, 2, 3, and 6 show hydride containers with water feed tubes.

Figure 4 is a block diagram of a hydrogen generator.

5   Figure 5 is a block diagram of a hydrogen generator and a metal regenerator.

Figures 7 and 8 are side sectional and top views of a hydrogen generation canister.)

The slurry

Hydrogen fuel can be stored in a medium that takes the form of a slurry. The slurry
includes a carrier liquid, such as an organic carrier, a dispersant, such as a triglyceride,

10   for stabilizing the slurry, and a chemical hydride dispersed in the carrier liquid at a
concentration of at least 40 and typically less than 75%, except for a dry, non-pumpable
slurry described later, in which the concentration may be higher. The best range can be
determined experimentally. Higher percentages yield higher energy densities. Lower
percentages are less viscous. A good tradeoff for a slurry of LiH with light mineral oil

15   and a triglyceride dispersant is about 61% of LiH. Above this percentage, the slurry
became too thick to pump. Higher concentrations may be achievable by replacing LiH
with MgH_2.

Typical slurries will be in the 50-70% range depending on the hydride used. LiH
slurries will likely be in the 50-61% range. A thinner slurry, with as little as 40%

20   hydride by weight of the slurry may be useful for certain applications.

The slurry may be safely stored and transported and the hydrogen may be easily
extracted for use as a fuel. The slurry is not highly flammable or combustible and may
be safely handled, stored, and transported. The slurry is stable at normal environmental
temperatures and pressures and, because it is a liquid, can easily be pumped through

conduits. The reaction rate with the slurry is easily controlled.

The carrier liquid

The carrier liquid may be an organic carrier liquid, such as mineral oil or a low
molecular weight hydrocarbon, such as an alkane, preferably pentane or hexane. A
5   preferable mineral oil is a non-toxic light mineral oil which exhibits a high flash point,
in the range of about 154 degrees C to about 177 degrees C and a viscosity in the range
of about 42 Saybolt Universal seconds (S.U.s.) to about 59 S.U.s.

The mineral oil is not chemically reactive with metal hydrides, produces relatively low
vapor pressure, and remains liquid through a temperature range of about -40 to 200
10   degrees C. The carrier liquid renders the slurry pumpable and, as a safe liquid, simple
to store or transport. The carrier slows the reaction rate when water is introduced into
the hydride. The use of a slurry permits easy refueling, as by simply topping off a tank.
Other carriers may work well, including carriers that are without water bonds and
preferably are without OH bonds. Silicone-based carriers may also work for slurries.
15   Light mineral oils have been tested successfully at percentages of 37 to 50% by weight
of the slurry.

The dispersant

The dispersant in the slurry may be, for example, a triglyceride dispersant, which
sterically stabilizes the slurry. The triglyceride dispersant preferably is triglyceride of
20   oleic acid, or triolein. Triolein is not normally considered to have the properties of a
dispersant. Other dispersants that could be used include Hypermer LP1, a polymeric
dispersant. One function of the dispersant is to attach to the particles of chemical
hydride, increasing the drag of the particle in the carrier fluid thus helping to prevent
settling. The dispersant also helps to keep the particles from agglomerating. The
25   dispersant promotes the formation of the slurry and the stabilization of the hydride into
the mineral oil.

Good dispersant concentrations range from 0.68% to 1.88% in tests. A particularly

good percentage is 0.75%. A broader range of percentages, from about 0.5 to about 2% of the slurry could be used. Instead of tryglicerides, the dispersants could be polymeric dispersants. A combination of triglyceride and polymeric dispersants may also be used, and may be particularly useful if the hydride is magnesium hydride.
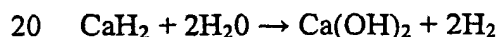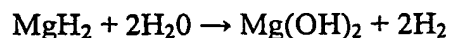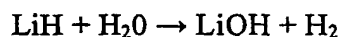
5   Dispersants sometimes have surfactant properties that may also be useful in the formation of the slurry.

The chemical hydride

U.S. Patent Application Serial No. 09/309,198, filed May 10, 1999, and incorporated by reference in its entirety, discloses hydrogen-containing material, such as lithium
10   hydride, lithium aluminum hydride, calcium hydride, sodium hydride, magnesium hydride, and others, for contact with a reactant, such as water, to produce hydrogen.

The chemical hydride in the slurry may be a light metal hydride, such as lithium hydride, lithium borohydride, lithium aluminum hydride, magnesium hydride, calcium hydride, sodium hydride, sodium borohydride, and sodium aluminum hydride, all of
15   which react with water to produce high purity hydrogen.

Examples of reactions are:

$$LiH + H_2O \rightarrow LiOH + H_2$$

$$LiBH_4 + 4H_2O \rightarrow LiOH + H_3BO_3 + 4H_2$$

$$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + 2H_2$$

20   $$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2$$

$$NaBH_4 + 4H_2O \rightarrow NaOH + H_3BO_3 + 4H_2$$

The hydrides are finely ground before being mixed with the other components of the slurry. The particles of the slurry are between 5 and 10 microns in diameter.

To make the slurry, we start with a powder form of hydride. This powder is first combined with a mixture of the mineral oil and dispersant. Then the mixture is ground in a grinder to further reduce the size of the particles. The final particles were measured to be primarily between 5 and 10 microns in diameter.

5   The hydrogen generation capability of the above hydrides when reacted with water is outstanding. For example, the volume of H_2 produced by complete hydrolysis of 1 kg. (2.2 lb.) of lithium hydride is 2800 liters (99 ft^3), and by complete hydrolysis of 1 kg of lithium borohydride is 4100 liters (145 ft^3).

Characteristics of the slurry

10   In summary, pumpable mixtures (slurries) can usefully have proportions of components that are 40-75% hydride (but see the later discussion concerning dry slurries having greater concentrations), 28-59.5% carrier, and 0.5 to 2% dispersant. A particularly good mixture is 60% lithium hydride, 0.75% triglyceride, and 39.25% light mineral oil.

Slurries of the kind described here (with hydride concentrations less than about 75%)
15   have a liquid-like flow characteristic and may be used in generation processes that involve continuous formation and extraction of hydrogen. In such processes, the slurry can be continuously introduced into a tank, while a portion of the slurry is continuously drawn off and subjected to water to release hydrogen. The reaction may be stopped and started quickly and repeatedly without sacrificing control of the reaction or safety.

20   The oil in the slurry protects the hydride from unintentional contact with moisture in the air and renders the hydride pumpable. The slurry, when in the form of a continuing stream, provides a path for dissipating heat generated from the hydride/water reaction. That, in conjunction with control of surface chemistry of the carrier liquid, permits easy control of the hydride reaction rate. In a continuous process, the hydrogen production
25   rate is controlled by the injection rate of water and hydride.

Because the oil inhibits water access to the hydride, it controls the rate of reaction, which otherwise could be explosive. The dispersant maintains the hydride particles in

9

suspension. The dispersant attaches to the particles and fends off adjacent particles to prevent agglomeration of the particles. The mineral oil protects the particles from unintentional reaction with water. The amount of the dispersant and the size of the hydride particles control the viscosity of the slurry.

5   The slurry burns only if high heat is applied, as by a blow torch, and maintained. Upon removal of heat, the burning of the slurry ceases and flames die out.

Alternative dry slurry

An alternative hydrogen storage medium would be in the form of a dry slurry comprising 90%-95% hydride. When a drop of water is injected into a mass of dry
10   slurry in a test tube, a volume of about 1 cubic centimeter of the hydride around the droplet reacts with the water, releasing hydrogen. Some of the water flashes to steam and the steam reacts with hydride as it escapes the tube with the released hydrogen.

As shown in figure 1, this effect can be exploited by packing dry hydride slurry 102 into a tube 100 and pulling a needle 104 (which had been placed in the tube when it
15   was packed) out of the tube while intermittently passing water droplets through the needle. Each water droplet would then strike fresh hydride until the needle is fully withdrawn.

As shown in figure 2, an alternate configuration would be to locate needles 106 strategically throughout (e.g., along the length of) a large mass of dry hydride or in
20   tubes 108 of hydride (only one tube is shown in figure 2). A valve 110 would then be controlled to selectively put water droplets into different parts of the mass or into different parts of the tube to produce hydrogen as required. This arrangement would have the advantage of requiring only one moving part, the valve, and would provide the opportunity to control where the heat is being generated and how the heat of reaction is
25   dissipated.

As shown schematically in figure 3, another configuration would use several parallel needles 120 with ends 122 located at different distances along the length of a tube of

hydride 124. As the water drops are supplied simultaneously to all of the needles of the set, hydride would be reacted along the tube at several locations. Then the set of needles would be moved outward 125 along the centerline 126 of the tube so that the ends 122 are in contact with new hydride slurry. This configuration reduces the

5   distance that must be traversed by any one needle. Because reacted hydride 128 will exist downstream of the lower needles, a path of egress 132 must be provided for the generated hydrogen and steam. The path could be provided by non-reacting porous material 130 positioned along the wall of the hydride tube far enough away from the centerline of the tube so that all the water vapor is consumed in reaction with hydride

10   before the gases reach the porous wall. Then only hydrogen would be conducted along the porous material to an outlet end 134.

The oil in the dry slurry coats the hydride particles and reduces the rates of reactions with the slurry.

The Hydrogen Generator

15   As shown in figure 4, a wet slurry can be used to generate hydrogen in a hydrogen fuel generation assembly 8 that includes a reservoir 10 for the slurry, a reservoir 14 for water, and a hydride reactor 18. The water and slurry are delivered by pumps 16, 12 to the reactor 18, which mixes the slurry and water to release hydrogen. A tank 26 receives the hydrogen and hydroxide waste from the reactor, and separates the

20   hydrogen from the hydroxide byproduct. A heat exchanger 32 receives the hydrogen (and associated water vapor) carried in conduit 30 from the tank and condenses the water.

A gas-liquid separator 40 receives hydrogen and water carried in line 34 from the heat exchanger, separates the water from the hydrogen, and dispenses dried hydrogen and

25   water in discrete streams 44, 42. (The water that is carried in conduit 34 is partly in droplet form, and partly in liquid stream form.) The water from the separator is conveyed to the water reservoir 14 (or to water flowing from the reservoir to the reactor) through conduits 42, 36, and the dried hydrogen is conveyed to a hydrogen-

fueled power-producing device 38, such as a fuel cell.

In figure 4, the hydride reactor 18 includes a tubular member 20 housing a mixing device, such as an auger 22, rotatable in the housing. Other mixing devices could also be used including ultrasonic mixers or vibratory mixers.

5   The amount of water pumped to the reactor 18 is more than is needed to complete the release of hydrogen from the slurry. The excess water is converted to steam and carries heat produced in the reaction out of the reaction chamber, thus controlling the temperature of the reaction.

The tubular member 20 may be fixed to, or otherwise in communication with an inlet
10   24 of the tank 26. In tank 26, the hydroxide solid material falls to the bottom 28 for removal by way of an outlet 29.

When the hydrogen-fueled power-providing device is a fuel cell 38, water condensed from the exhaust of the fuel cell is also returned to the water reservoir 14, or to the water flowing from the reservoir to the reactor.

15   When the hydrogen-fueled power-providing device 38 is an internal or external combustion engine, the assembly also includes a condenser 46 that accepts water vapor from the device 38 through a conduit 48 and condenses water. The condensed water passes through conduit 50 into the conduit 38 for return to the water reservoir 14 (or water flowing from the reservoir into the reactor 18).

20   Thus, hydrogen suitable for use with fuel cells or engines, for example, is generated by providing a slurry including an organic carrier liquid, such as a light mineral oil, a triglyceride dispersant, and a chemical hydride, such as lithium hydride, mixing the slurry with water to release hydrogen from the slurry, controlling the reaction temperature by vaporization of water, condensing water from the hydrogen released
25   from the slurry, and conveying the dried hydrogen to the hydrogen-fueled power-producing device.

The slurry may be prepared at centralized plants, where it is readily pumpable into tank trucks or through pipes to distribution centers where the slurry can be pumped into tanks of vehicles powered by hydrogen fuel cells, or into slurry reservoirs of homes or business and industrial facilities. The hydroxide byproduct of the hydrogen production

5   reaction may be picked up upon the next delivery of slurry is made and transported back to a regeneration plant, where the hydroxide will be separated from the mineral oil and will be regenerated to hydride, as explained below.

Other techniques for distributing water to the hydride

As shown in figure 6, another method of distributing water to the hydride in a chamber

10   is through needles placed in hydride tubes in locations that permit water droplets that pass through needles to react with enough of the hydride to release more than 90% of the potential hydrogen. Several needles could be placed along the length of each tube. Water would be delivered first to the needle 154 that is farthest from the exit of the tube 156. This water would react with the hydride around it. Some of the water would be

15   evaporated and would travel through unreacted hydride causing further reaction along the tube. A valving system 158 would be incorporated with the tubes of hydride to deliver water to the needles selectively. A computer control system 160 would record which needles had already delivered water and would select needles that had not delivered water for future hydrogen release.

20   The system of figure 6 overcomes the blockage of water and hydrogen flow to all portions of hydride by the metal hydroxide byproduct that is formed during the reaction. By selecting the sequence of tubes and needles for water injection, water is delivered only to fresh hydride. The arrangement of figure 6 also allows the heat released from the reaction in one tube to be dissipated from the tube while another tube

25   in the system is reacting with water to deliver hydrogen. By causing the reactions to occur in different tubes, the heat of reaction on one tube can dissipate to the environment while slurry and water are reacting in another tube to continue to produce hydrogen. The system may be designed so that the heat in one tube is dissipated before

another reaction must take place in that tube. This will control the temperature of the tube and the materials within the tube.

Alternatively, the needles could be retractable from the tubes in a manner similar to that shown in figure 3.

5   *Small scale implementation*

In a small scale implementation, shown in figures 7 and 8, the water supply tubes 170 are buried in a bed 172 of chemical-hydride slurry in such a manner that each supply tube will provide enough water to react with the chemical hydride near the outlet 174 of the tube. Water is stored in chambers 176 located around the perimeter of a canister 180

10   that holds the lithium hydrid tubes 182. A valve 177 sequentially directs charges of water to each successive region of chemical hydride. The valving mechanism could be based on inkjet technology. Water charges would be supplied when the pressure in the canister drops below a set value. In this manner, the pressure in the canister will be cycled between a high value of about 200 psi and a low value of about 50 psi. The

15   generated hydrogen exits the canister through conduit 183 after passing through a carbon filter 184.

The hydrogen produced could be consumed by an attached fuel cell as fast as it is generated and the electricity produced by the fuel cell may be stored in a battery or capacitor.

20   By supplying discrete charges of water sufficient to react with the chemical hydride within a specified diameter of the release location, the reaction within the canister176 can be controlled so that there is never a surplus of water. As the chemical hydride reacts with water, its volume increases. This increased volume occupies the storage volume of the water that is consumed, to achieve a minimum system volume. Flexible

25   walls 190 enable the water supply chambers and the hydride tubes to change volume as needed.

The Hydrogen Regenerator

The hydroxide byproduct can be processed to regenerate its elemental metal component. The metal can then re-used in the hydride fuel generating process by hydrogenating the elemental metal to produce the hydride fuel.

5   As shown in figure 5, the hydrogen generation assembly is similar to the one shown in figure 4 and includes a reactor 210 and inlet tubes 212, 214 which convey slurry and water, respectively, to the reactor 210. The reactor 210 includes a tubular portion 216 housing an auger 218 for mixing the slurry and water to effect release of hydrogen gas (H_2) from the slurry. A reactor tank portion 219 receives the hydrogen gas and solid

10   matter from the auger 218. The hydrogen gas moves toward a top portion 220 of the reactor tank portion 219 and is carried by a conduit 222 to a separator (not shown) for drying the hydrogen. The hydroxide, which is a wet solid dust 224, falls to a bottom portion 226 of the reactor tank portion 219, from which it is removed and conveyed by transport means 223 to a mixer 228. Mixer 228 receives carbon through a conduit 234

15   and mixes the carbon with the hydroxide. The conduit 234 introduces the carbon, in solid or fluid form, such as coal in pellet or powder form, biomass, or graphite, to the mixer 228. The mixed carbon and hydroxide are transported by transport 229 to a second reactor 230 where there is disposed a molten pool 232 of carbon dissolving metal, such as iron, nickel, manganese, and alloys of those metals. The metal, because

20   of its high heat capacity and thermal conductivity, provides superior heat transfer characteristics.

Alternatively, the mixer 228 may be omitted and the carbon and hydroxide fed directly into the reactor 230.

The intermixed carbon and hydroxide particles form a layer 238 in the reactor 230, the

25   layer 238 descending into a layer 236, and then sinking into the pool of molten carbon dissolving metal 232. In layer 236, decomposition of hydroxide into oxide and water vapor occurs. In layer 232, the reaction between carbon and metal oxide produces

elemental metal and carbon monoxide.

In one example, the hydroxide is lithium hydroxide (LiOH) and the carbon-dissolving metal is iron (Fe). The lithium hydroxide and carbon introduced into the second reactor 230, forms the upper layer 328 which descends in the reactor 230 and in the area of

5   layer 236 produces lithuim oxide (Li_2O), water (H_2O), hydrogen (H_2) and carbon monoxide (CO). The hydrogen (H_2) and carbon monoxide (CO) rise toward the top of the reactor 230. Lithium oxide (Li_2O) and carbon (C) sink into the molten pool of iron (Fe) where they produce lithium metal (2Li), carbon monoxide (CO) and iron. (Fe).

In the molten layer 232, lithium gas (Li) is also produced, which rises to the second

10 reactor upper portion 238. Liquid lithium (Li) and iron (Fe) pass from the second reactor metal pool 232 to a separator 240 through a conduit 242. The gaseous lithium (Li) in the upper portion 238 of the reactor 230, along with hydrogen (H_2) and carbon monoxide (CO), pass through a conduit 246 to a condenser 244. Condenser 244 separates out carbon, lithium, and lithium oxide, which, in solid/liquid form, pass into

15 the separator 240 through a conduit 248. The condenser 244 discharges carbon monoxide and hydrogen gas through a conduit 250 to another separator 258, which separates the carbon monoxide from the hydrogen.

In the separator 240, the lithium (Li) is evaporated and released through conduit 252 in vapor form, while the lithium oxide (Li_2O), in liquid form, is passed through conduit

20 254 to the molten metal pool 232 in the second reactor 230. The lithium discharged by the separator 240 and the hydrogen discharged by the separator 258 may be recycled for use in the hydride slurry.

Pumps may be used in the assembly as needed. For example, the conduits 242, 254 may have magneto-hydrodynamic pumps for pumping molten metal. The molten metal

25 pool 232 may be maintained at a temperature of at least 1500° Kelvin, somewhat above the melting temperature of carbon saturated iron (1430°K). Alloys can be used to tailor the temperature.

The operating temperature of the second reactor 230 is maintained lower than would otherwise be required by continuously introducing into the molten pool 232 an inert gas, such as argon, through an inlet 256. The lithium concentration in the lower layer 232 of the reactor 230 is thus maintained at a low level. The continuous use of the inert

5   gas tilts the thermodynamic equilibrium in favor of the lithium, allows the operating temperature to be reduced significantly and achieves higher yields at lower temperatures. Without the inert gas, the second reactor 230 would have to be maintained at about 1850°K to obtain the same yield as 1500°K with the inert gas. The temperature in the second reactor 230 may also be influenced by using an iron alloy

10   such as iron-manganese (FeMn).

When the carbon components are introduced directly into the reactor 230, they may include natural gas, which is flowable into the reactor 230 through inlet 256 or a similar inlet.

In accordance with a further feature of the invention, there is provided a method for

15   converting metal oxides and hydroxides to the elemental metals thereof.

The assembly and method provide for a substantially closed-loop conversion, without discharge of harmful elements into the atmosphere.

Other embodiments are within the scope of the following claims.

For example, elemental metals other than lithium may be recovered, such as sodium

20   and potassium. Alkaline-earth metals, such as magnesium and calcium, could also be recovered.

CLAIMS

1.   A composition comprising

a carrier liquid;

a dispersant ; and

5   a chemical hydride..

2.   The composition of claim 1 in which the chemical hydride has a concentration of at least 40% by weight of the composition.

3.   The composition of claim 1 in which the chemical hydride has a concentration of less than 75% by weight of the composition.

10   4.   The composition of claim 1 in which the chemical hydride has a concentration of about 61% by weight of the composition.

5.   The composition of claim 1 in which the chemical hydride has a concentration of more than 90% by weight of the composition.

5.   The composition of claim 1 in which the carrier liquid comprises an organic

15   liquid.

6.   The composition of claim 5 in which the organic liquid comprises mineral oil.

7.   The composition of claim 6 in which the organic liquid comprises a light mineral oil.

8.   The composition of claim 1 in which the carrier liquid comprises a

20   hydrocarbon.

9.   The composition of claim 8 in which the hydrocarbon comprises an alkane.

10.   The composition of claim 9 in which the alkane is selected from a group

consisting of pentane and hexane.

11.   The composition of claim 1 in the form of a slurry.

12.   The composition of claim 1 in which the carrier liquid has a viscosity in the range of about 32 Saybolt Universal seconds (S.U.s.) at standard temperature and

5   pressure (STP) to about 100 S.U.s, preferably about 42 S.U.s. to about 59 S.U.s.

13.   The composition of claim 1 in which accordance with the carrier liquid exhibits a flash point in the range of about 100 °C to about 350 °C, preferably about 154°C to about 177°C.

14.   The composition of claim 1 in which the chemical hydride comprises a light

10   metal hydride.

15.   The composition of claim 1 in which the light metal hydride is selected from the group consisting of lithium hydride, lithium borohydride, lithium aluminum hydride, sodium hydride, sodium borohydride, sodium aluminum hydride, magnesium hydride, and calcium hydride.

15   16.   The composition of claim 1 in which the dispersant comprises a triglyceride.

17.   The composition of claim 16 in which the triglyceride acts as a dispersant.

18.   The composition of claim 1 in which the triglyceride comprises a triglyceride of oleic acid.

19.   The composition of claim 1 in which chemical hydride comprises lithium

20   hydride.

20.   The composition of claim 1 in which chemical hydride comprises magnesium hydride.

21.   A method comprising the mixing of the chemical hydride with a mixture of the carrier liquid and a triglyceride after which the resulting mixture if further ground to

form a stable slurry.

22.   A composition comprising

a mass of chemical hydride particles in a concentration of about 90-95% by weight of the composition, and

5   oil coating the chemical hydride particles, the oil comprising 5-10% by weight of the composition.

23.   Apparatus comprising:

a reservoir containing a chemical hydride, and

a mechanism configured to introduce a reactant to selected different portions of
10   the chemical hydride to effect hydrogen generating reactions at different locations within the reservoir.

24.   The apparatus of claim 23 in which the reservoir comprises a canister.

25.   The apparatus of claim 23 in which the reservoir includes chambers that contain chemical hydride.

15   26.   The apparatus of claim 23 in which the mechanism comprises conduits that have open delivery ends arranged to introduce the reactant to respective selected portions of the chemical hydride.

27.   The apparatus of claim 23 in which the conduits are arranged in parallel.

28.   The apparatus of claim 27 in which the conduits are located at different
20   distances along an axis of the reservoir.

29.   The apparatus of claim 23 in which the mechanism is configured to be movable relative to the chemical hydride contained in the reservoir.

30.   The apparatus of claim 16 in which the conduits comprise needles.

31.   The apparatus of claim 23 in which the mechanism includes a valving system that controls the introduction of the reactant to the different portions.

32.   The apparatus of claim 23 in which the reservoir includes an exit for hydrogen
5   generated in the reaction.

33.   The apparatus of claim 23 in which the chemical hydride is dispersed in a carrier liquid at a concentration of about 40-75% by weight of the composition.

34.   The apparatus of claim 23 in which the carrier liquid comprises an organic liquid.

10   35.   The apparatus of claim 23 in which the chemical hydride comprises a light metal hydride.

36.   The apparatus of claim 35 in which the light metal hydride is selected from the group consisting of lithium hydride, lithium borohydride, lithium aluminum hydride, sodium hydride, sodium borohydride, sodium aluminum hydride, magnesium hydride,
15   and calcium hydride.

37.   The apparatus of claim 33 also including a triglyceride acting as a dispersant.

38.   The apparatus of claim 23 in which chemical hydride comprises lithium hydride.

39.   The apparatus of claim 23 in which chemical hydride comprises magnesium
20   hydride.

40.   The apparatus of claim 23 in which the reactant comprises water

41.   A hydrogen fuel generation assembly comprising:

a reservoir for a slurry comprising a carrier liquid, a triglyceride dispersant, and a chemical hydride;

25   a reservoir for water;

a hydride reactor in communication with said slurry reservoir and said water reservoir and adapted to receive the slurry and water from the reservoirs, respectively, and to mix the slurry and water to effect release of hydrogen from the slurry;

a tank for receiving the hydrogen from said reactor and for receiving hydroxide

5   byproduct from said reactor, and for facilitating separation of the hydrogen and the hydroxide byproduct;

a heat exchanger for receiving the hydrogen from said tank and adapted to condense water from the hydrogen;

a gas-liquid separator for receiving hydrogen and water from said heat exchanger and

10   adapted to separate the water from the hydrogen and to dispense dried hydrogen;

a conduit for conveying the water from said separator to said water reservoir; and

a conduit for conveying the dried hydrogen to a hydrogen-fueled power-producing device.

42.   The assembly of claim 41 wherein said reactor comprises a tubular housing and

15   a mixer for mixing the slurry and the water.

43.   The assembly of claim 41 wherein said tank is provided with an outlet for flowing hydrogen gas from the tank, and a bottom portion for the receiving of the hydroxide byproduct.

44.   The assembly of claim 41 further comprising the power-producing device.

20   45.   The assembly of claim 44 wherein said power-producing device comprises a selected one of a fuel cell, an internal combustion engine, and an external combustion engine.

46.   The assembly of claim 45 wherein said power producing device comprises a fuel cell, and further comprising conduit means for conveying condensed water from

said fuel cell to said water reservoir.

47.   The assembly of claim 45 wherein said power-producing device comprises a selected one of the internal combustion engine and the external combustion engine and the assembly further comprises a condenser for condensing water from water vapor

5   from said engine, said condenser being in communication with means for conveying water from said condenser to said water reservoir.

48.   A method for generating hydrogen fuel for a power-producing hydrogen-fueled device, the method comprising the steps of:

providing a slurry comprising an organic carrier liquid, a triglyceride dispersant, and a

10   chemical hydride;

mixing said slurry with water to effect release of hydrogen from the slurry;

removing water vapor from the hydrogen released from the slurry, to provide dried hydrogen; and

conveying the dried hydrogen to the hydrogen-fueled device for the production of

15   power.

49.   The method of claim 48 wherein said organic carrier liquid comprises a light mineral oil.

50.   The method of claim 48 wherein said chemical hydride comprises a selected one of lithium hydride, lithium borohydride, a combination of lithium hydride and

20   lithium borohydride, lithium aluminum hydride, sodium hydride, sodium borohydride, sodium aluminum hydride, magnesium hydride, and calcium hydride.

51.   The method of claim 48 wherein said chemical hydride comprises lithium hydride.

52.   The method of claim 48 wherein said mixing of said slurry and said water is

undertaken with an auger.

53.   The method of claim 48 wherein said mixing of said slurry and said water is undertaken with an ultrasonic mixer.

54.   The method of claim 48 comprising the further step of flowing the water
5   removed from the hydrogen back to a source of the water for mixing with the slurry.

55.   The method of claim 48 wherein the hydrogen-fueled device comprises a fuel cell, the method comprising the further step of flowing water condensed from the fuel cell back to a source of the water for mixing with the slurry.

56.   A regeneration assembly for converting metal oxides and hydroxides to
10   elemental metals, the assembly comprising:

a reactor adapted to receive the metal hydroxide and carbon, and adapted to retain a molten carbon-dissolving metal in the reactor;

means for flowing gases comprising the elemental metal in gaseous form, carbon monoxide, and hydrogen from said reactor;

15   a condenser adapted to receive the gases flowed from said reactor and adapted to discharge carbon monoxide and hydrogen from a first outlet and the elemental metal, metal oxide, and carbon from a second outlet;

a separator adapted to receive the elemental metal, oxide thereof, and carbon from said condenser and to discharge the elemental metal in gaseous form;

20   means for flowing the elemental metal and the carbon dissolving metal in liquid form from said reactor to said separator; and

means for flowing the metal oxide and the carbon dissolving metal from said separator to said reactor.

57.   The assembly of claim 56 further comprising a second separator for receiving

the carbon monoxide and hydrogen from said condenser, said second separator having a first outlet for discharging carbon monoxide and a second outlet for discharging hydrogen.

58.   A method for converting metal oxides and metal hydroxides to elemental metals
5   thereof, the method comprising the steps of:

admitting the metal hydroxide and carbon into a reactor having molten carbon-dissolving metal therein;

flowing gases comprising the elemental metal in gaseous form, carbon monoxide and hydrogen from the reactor to a condenser;

10   condensing out the elemental metal and oxide thereof, and carbon, and flowing same to a separator;

flowing carbon monoxide and hydrogen from the condenser;

flowing the elemental metal and the carbon dissolving metal from the reactor to the separator;

15   flowing elemental metal oxide and the carbon dissolving metal from the separator to the reactor; and

flowing the elemental metal from the separator.

59.   The method of claim 58 including the further step of flowing an inert gas into the reactor.

20   60.   A composition comprising

a carrier liquid;

a triglyceride; and

a chemical hydride dispersed in the carrier liquid at a concentration of about 40-75% by

weight of the composition.

61.   The composition of claim 1 in which the triglyceride comprises triolein.

62   The apparatus of claim 23 in which the chemical hydride is dispersed in a
carrier liquid at a concentration about 90-95% by weight of the composition.
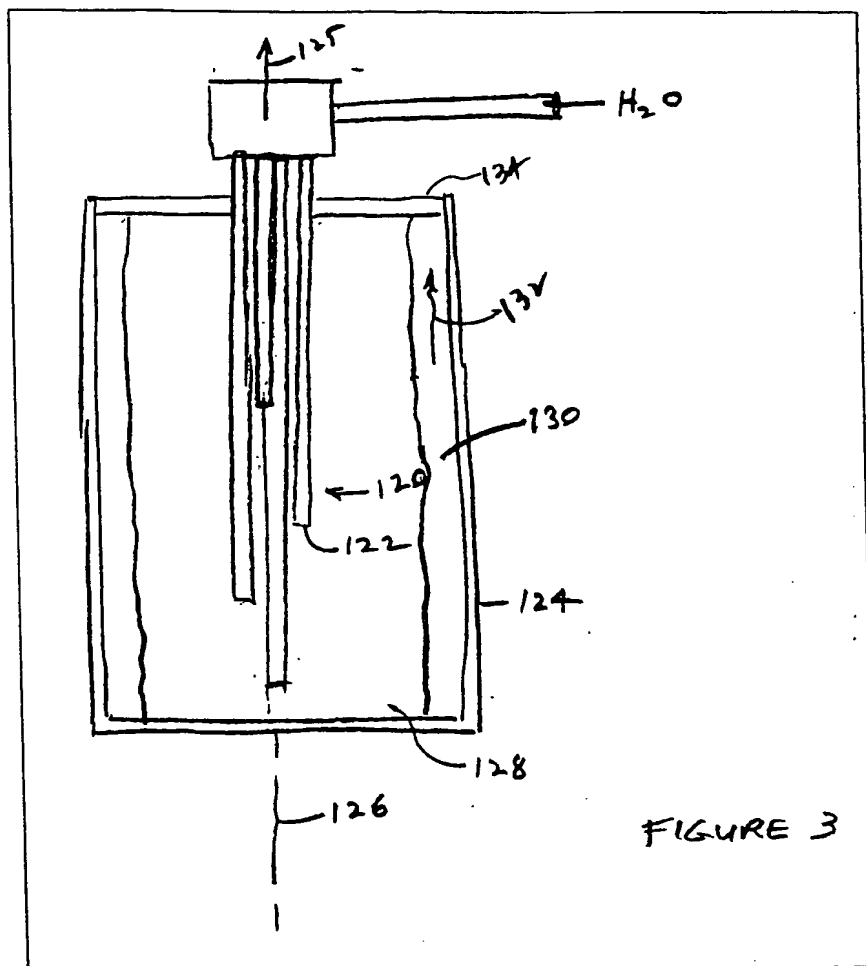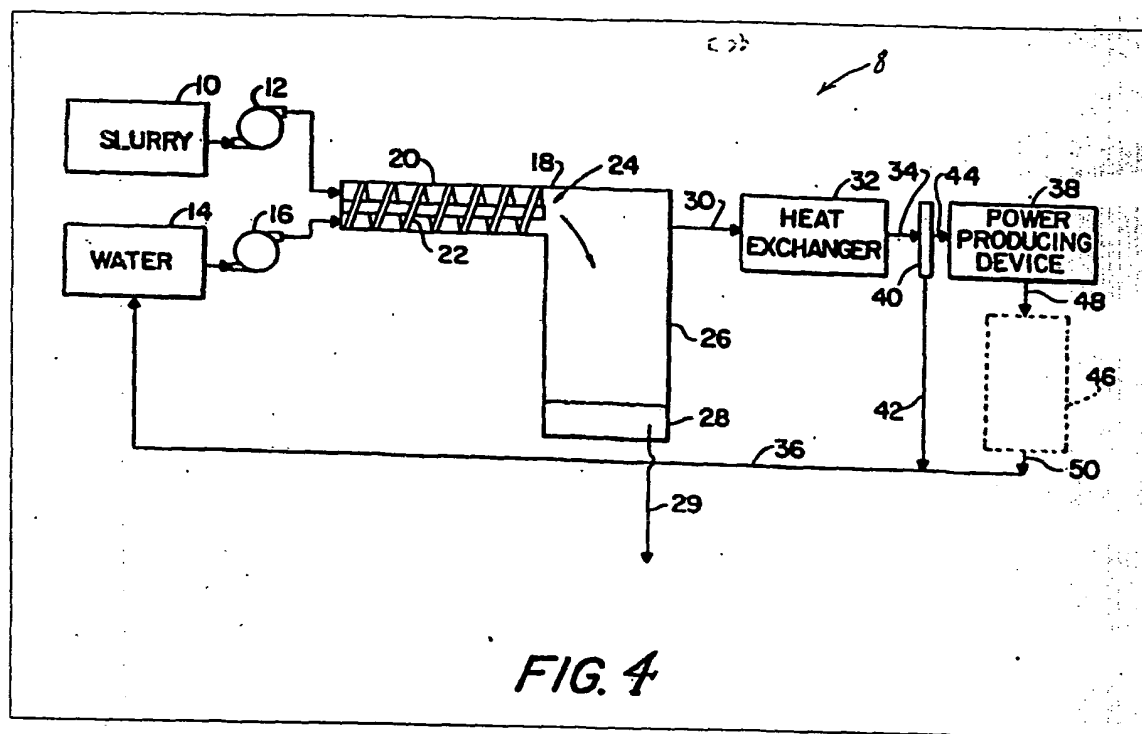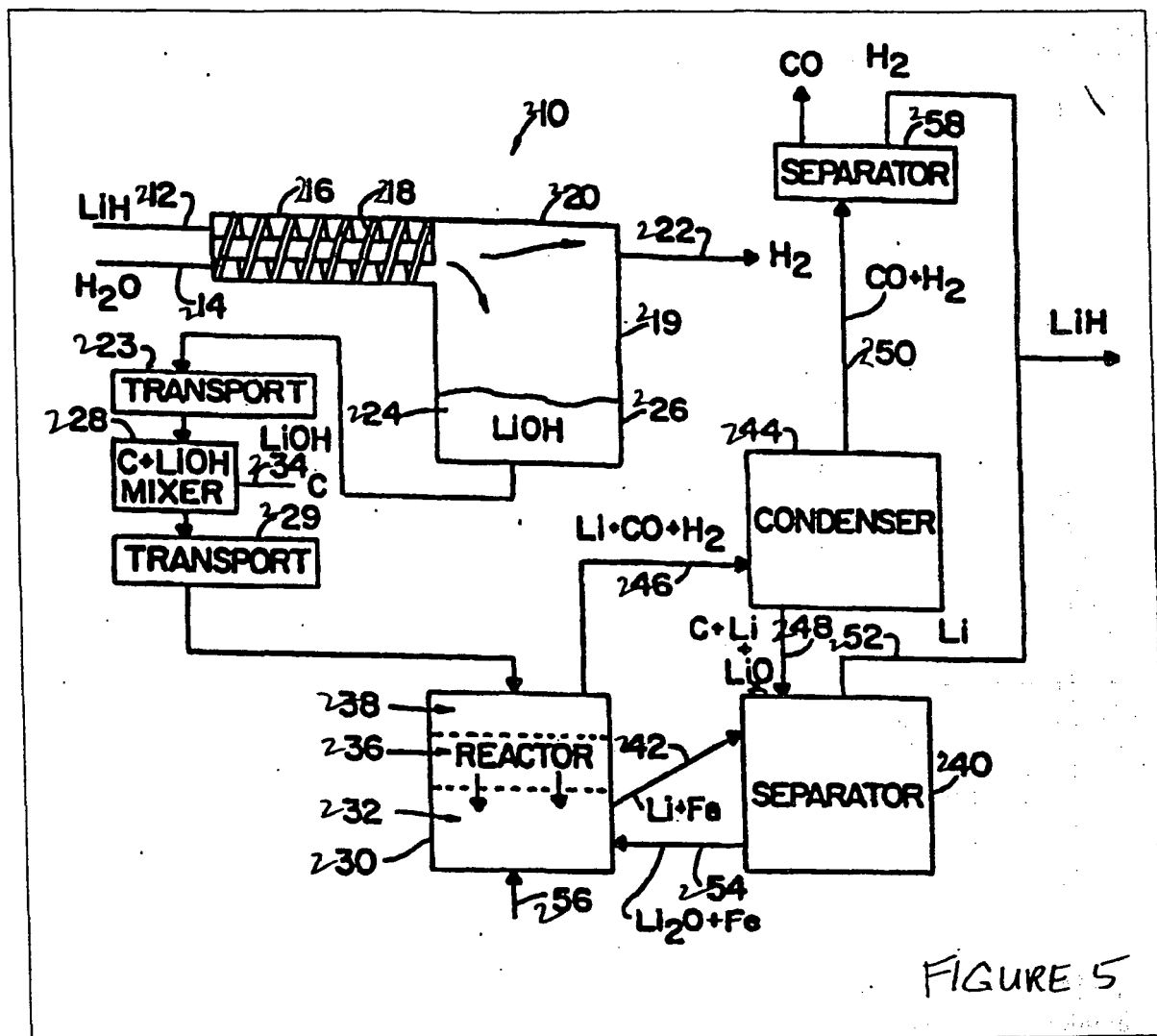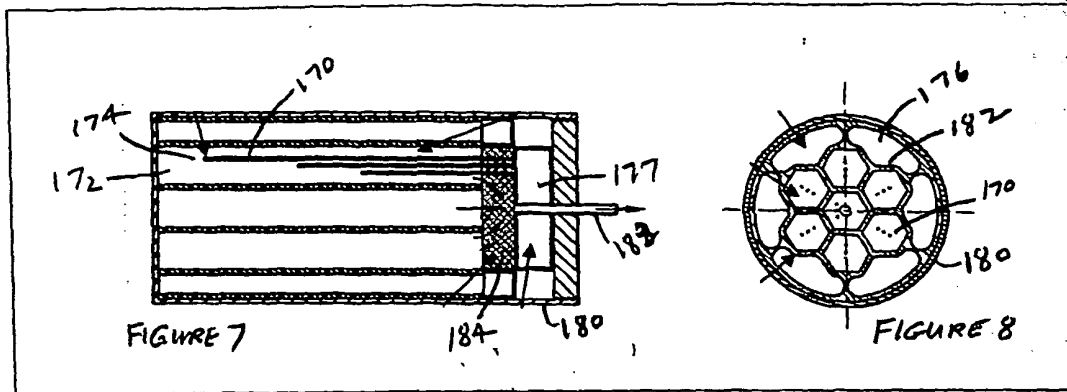
FIGURES

104

H₂O

102

100

FIGURE 1.

H₂O

VALVE

110

106

108

FIGURE 2

60

158

150

152

156

154

FIGURE 6

FIGURE 3

FIG. 4
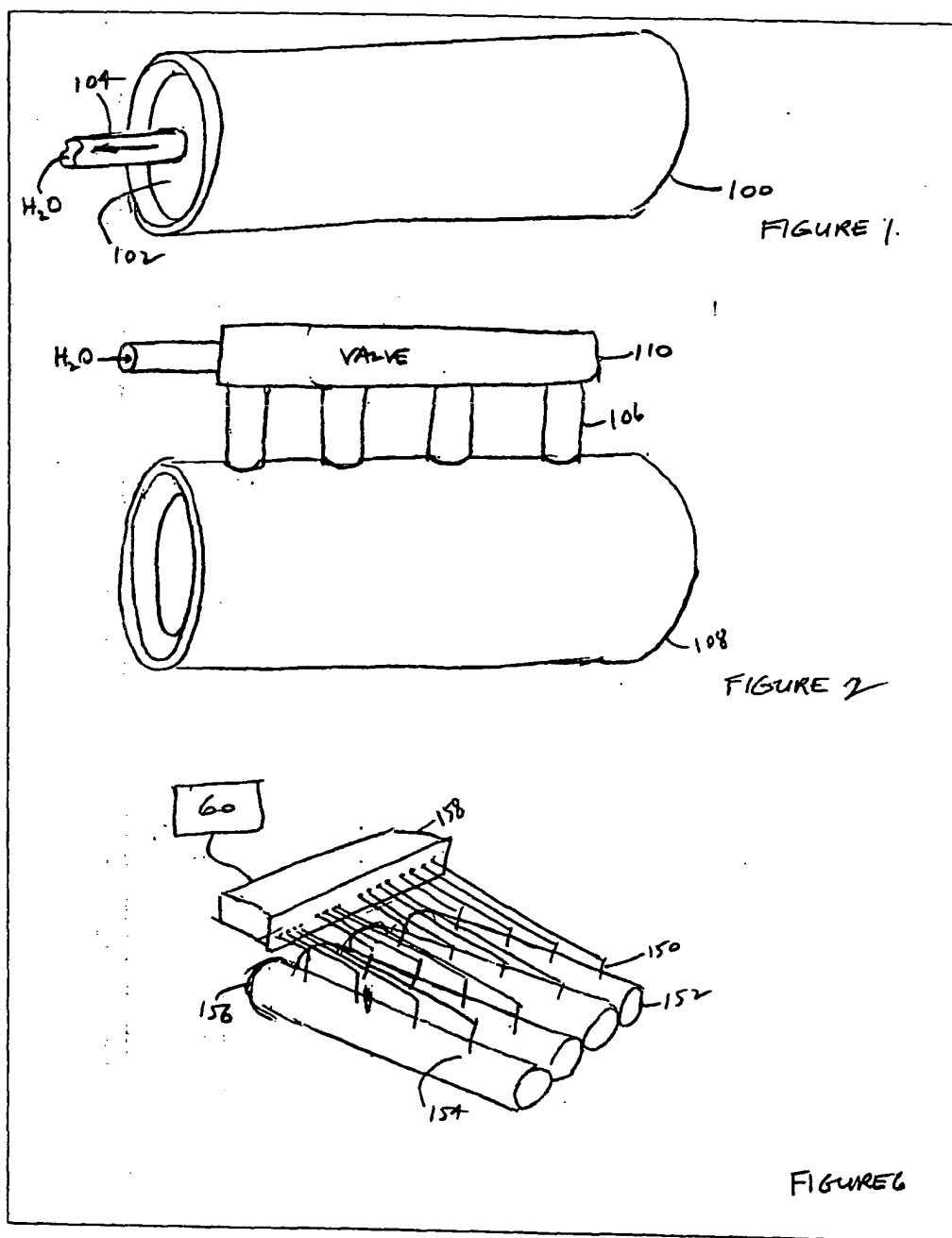
FIGURE 5

FIGURE 7

FIGURE 8

5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US02/00923

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7)   :C01B 3/08, 6/04, 6/24; B01J 7/00
US CL   : 252/188.25,182.32; 423/657, 646; 422/239; 48/4,61

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :   252/188.25, 182.32, 188.26, 188.27; 423/657, 646, 647; 422/239, 238, 232, 233, 236, 261; 48/4, 61,

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST USPAT TEXT SEARCH

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,759,986 A (CREGER et al.) 18 September 1973, see abstract and column 9, lines 4-41.	1-16, 20-21 and 23
X	US 5,468,880 A (UENO et al.) 21 November 1995, see abstract, and examples 11-13.	1-16, 20-21, 23
X --- A	US 5,707,499 A (JOSHI et al.) 13 January 1998, see abstract, and figures, such as figure 5	24-48, 63 ------ 57-59
X --- Y	US 5,867,978 A (KLANCHAR et al.) 09 February 1999, see abstract, figures, and claims.	24-33, 36-37, 39-41 ---- 1-23, 34-35, 38, 42-56, 60-63

| X | Further documents are listed in the continuation of Box C. | ☐ | See patent family annex. |

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"A"   document defining the general state of the art which is not considered to be of particular relevance

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"&"   document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29 MAY 2002	2 7 JUL 2002

Name and mailing address of the ISA/US	Authorized officer
Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	JOSEPH D. ANTHONY
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 3,975,913 A (ERICKSON) 24 April 1976, see abstract, figures, and claims.	24-33, 36-37, 39-41 ---------- 1-23, 34-35, 38, 42-56, 60-63
X --- A	US 3,674,702 A (MACKENZIE et al.) 04 July 1972, see abstract, column 3, lines 1-30 and example 1.	23 --- 57-59
X ---- Y	US 4,261,955 A (BAILEY, JR. et al.) 14 April 1981, see abstract and figures.	24-28, 30, 33, 36-37, 39-41 ------- 1-23, 29, 31-32, 34-35, 42-56, 60-62
Y --- A	US 3,649,360 A (BLOOMFIELD et al.) 14 march 1972, see abstract, figures, and claims.	1-56, 60-63 -------- 57-59

XP-001028503

AN ULTRASAFE HYDROGEN GENERATOR
AQUEOUS, ALKALINE BOROHYDRIDE SOLUTIONS AND Ru CATALYST

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ABSTRACT

A novel, simple, convenient, and safe, chemical process generates high purity hydrogen gas on demand from stable, aqueous solutions of sodium borohydride, $NaBH_4$, and ruthenium based (Ru), catalyst. When $NaBH_4$ solution contacts Ru catalyst, it spontaneously hydrolyzes to form H_2 gas and sodium borate, a water-soluble, inert salt. When H_2 is no longer required, Ru is removed from the solution and H_2 generation stops. Since this H_2 generator is safer, has quicker response to H_2 demand, and is more efficient, than commonly used H_2 generators, it is ideal for portable applications.

INTRODUCTION

PEM fuel cells are attractive power sources for providing clean energy for transportation and personal electronics applications where low system weight and portability are important. For powering these systems, H_2 gas is the environmentally desirable anodic fuel of choice since only water is formed as a discharge product. A major hurdle is how to generate/store controlled amounts of H_2 fuel directly without resorting to high temperature reformers with significant heat signatures or bulky, pressurized cylinders.

Background of the Borohydride H₂ Generator

Our safe, portable H_2 generator overcomes these problems by using aqueous, alkaline, sodium borohydride ($NaBH_4$, tetrahydroborate) solutions which are extremely stable, as found by Schlesinger et al. (1), in the presence of selected metal (or metal boride) catalysts, this solution hydrolyzes to yield H_2 gas and water-soluble, sodium metaborate, $NaBO_2$.

$$NaBH_4 + 2 H_2O \xrightarrow{\text{catalyst}} 4 H_2 + NaBO_2 \qquad [1]$$
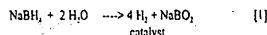
This hydrolysis reaction occurs at different rates depending on the catalyst used and its preparation method. Levy et al. (2) and Kaufman and Sen (3) investigated cobalt and nickel borides as catalysts for practical, controlled generation of H_2 from $NaBH_4$ solutions. We studied ruthenium (Ru) based catalyst supported on ion exchange resin beads. Using Ru is based on the work of Brown and Brown (4), who investigated various metal salts and found that ruthenium and rhodium salts liberated H_2 most rapidly from borohydride solutions. We chose Ru because of its lower cost. Ru catalysts are not consumed during hydrolysis and are reusable. We have designed our system so that reaction [1] is either self- regulating or carefully controllable. To generate H_2, $NaBH_4$ solution is allowed to flow onto a Ru catalyst, or $NaBH_4$ solution is injected onto Ru catalyst. This ensures fast response to H_2 demand i.e. H_2 is generated only when $NaBH_4$ solution contacts Ru catalyst. When H_2 is no longer needed, $NaBH_4$ solution is removed from Ru catalyst and H_2 production ceases. With molecular weights of $NaBH_4$ (38) and 2 H_2O (36), forming $4H_2$ (8), reaction [1] has a H_2 storage efficiency of 8/74 = 10.8%.

In addition to H_2, the other discharge product, $NaBO_2$, commonly found in laundry detergents, is safe. Unlike phosphates, borates are not environmentally hazardous in water supplies. Table 1 compares operational and safety features of generating H_2 via base-stabilized $NaBH_4$ solutions and via reactive chemical hydrides. Our generator is considerably safer/more efficient than producing H_2 via other reactive chemicals. The heat generated by our system (75 kJ/mole H_2 formed), is less than what is produced by other hydrides (>125 kJ/mole H_2), and ensures a safe, controllable chemical reaction.

The total amount of H_2 produced by reaction [1] depends on $NaBH_4$ solution volume and concentration H_2 generation rates are primarily a function of Ru catalyst active surface area H_2 pressure/flow rates can be accurately controlled and made self-regulating by numerous feedback

mechanisms. An added attribute of our generator is that generated H_2 gas also contains water vapor. Since prehumidified H_2 is needed in PEM fuel cells, $NaBH_4$ based H_2 generators should increase PEM fuel cell performance.

Experimental

Ru catalyst supported/dispersed on anionic exchange resin beads was prepared by ion exchange. Appropriate amounts of $RuCl_3 \cdot 3H_2O$ were dissolved in deionized water and acidified with HCl to convert $RuCl_3$ into $[RuCl_6]$. This H_3RuCl_6 solution was added to a weighed amount of anionic and cationic exchange resin beads which had been previously washed and dried at 50°C. The resulting slurry was allowed to stand at ambient temperature for 24 hours while stirring at regular intervals to maintain uniformity. The slurry was then dried by evaporation at 50°C. After drying, H_3RuCl_6, now impregnated in the resin, was reduced by addition of 20% $NaBH_4$, 15% NaOH, 65% H_2O solution. As prepared, our catalyst may be either metallic Ru or Ru boride of the form Ru_2B. The black, Ru coated resin beads were washed, dried, and separated with a 40 mesh sieve. Ru loadings were ~5% by weight.

In typical H_2 generation experiments ~30 ml of 20% $NaBH_4$ solution containing 10% NaOH was thermostated in a sealed flask fitted with an outlet tube for collecting evolved H_2 gas. Ru coated resin beads, were placed in a stainless steel screen container and dropped into the solution to begin H_2 generation. $NaBH_4$ solution could contact Ru catalyst through the screen. H_2 could exit, while lightweight resin beads were prevented from floating to the top of the solution. Although solutions were thermostated, temperatures near the catalyst were certainly higher due to the exothermic reaction. The outlet tube exhaust was placed under an inverted, water filled, graduated cylinder situated in a water-filled tank. Generated H_2 was measured by monitoring water displaced from the graduated cylinder as the reaction proceeded.

Results and Discussions

We evaluated anionic and cationic exchange resin beads as catalyst supports for Ru catalyst. Table 2. lists normalized H_2 generation rates for various ion exchange resin beads. Catalyst supports were evaluated based on their H_2 generation rates in liters H_2 generated/sec.-gram catalyst. This convenient standard meaningfully compares catalyst supports in our system because Ru catalyst performances are normalized with respect to catalyst weight. Table 2 illustrates that for catalytically generating H_2 from $NaBH_4$ solutions with ~5% Ru supported on ion exchange resins, anionic resins are better than cationic resins. A-26 and IRA-400 (Rohm and Haas) anion exchange resins when used as supports for Ru gave the highest H_2 generation rates.

Figure 1 plots H_2 volumes generated as a function of time for ~0.25 grams combined weight of Ru supported on IRA-400 anion exchange resin beads immersed in 20% $NaBH_4$, 10% NaOH, and 70% H_2O (wt %) solution at various temperatures. Volumes of H_2 generated by Ru catalyzed $NaBH_4$ hydrolysis increased linearly with time:

$$-4d[NaBH_4]/dt = d[H_2]/dt = k \qquad [2]$$

Under our experimental conditions of relatively high $[BH_4]$ and low catalyst weights (and surface area), k is constant for a given temperature. This example of zero order kinetics implies that the first step in reaction [1] involves a surface reaction, most likely BH_4^- adsorption on Ru catalyst. We have observed zero order kinetics for $NaBH_4$ hydrolysis even at $[NaBH_4]$ as low as 0.1%. Catalyzed $NaBH_4$ hydrolysis ultimately depends on $NaBH_4$. It would therefore not be surprising if diffusion controlled, first order kinetics dominates at very low $[NaBH_4]$ and/or high catalyst weights where catalyst sites are not totally occupied. From the data in Fig. 1, an activation energy for Ru catalyzed hydrolysis of $NaBH_4$ (obtained by plotting log [H_2 generation rate] vs reciprocal absolute temperature, 1/T), was computed to be 47 kJ mole^{-1}. This value compares with activation energies found (3) for $NaBH_4$ hydrolysis catalyzed with other metals: 75 kJ mole^{-1} for Co, 71 kJ mole^{-1} for Ni, and 63 kJ mole^{-1} for Raney Ni.

As reaction [1] proceeds, $NaBO_2$ eventually exceeds its solubility limit and precipitates out of solution. We were concerned that this solid may block catalyst sites thereby affecting subsequent H_2 generation rates. To test this, 5 ml. of $NaBH_4$ solution was catalytically hydrolyzed to completion and the total generated H_2 measured. Although H_2 generation rates slowed as the reaction proceeded, nevertheless, >70% of the stoichiometric amount of H_2 was generated based on the amount of $NaBH_4$ in solution. This indicated that reaction [1] is quite efficient and that $NaBO_2$ precipitation at these concentrations/conditions does not seriously interfere with catalyst operation. If water generated by PEM fuel cells could be returned to $NaBH_4$ solutions, additional H_2 could be generated because $NaBO_2$ would remain in solution.

865

We can estimate achievable power levels from our H_2 generator. Assuming a standard PEM fuel cell operates at ~0.7V, generating 1 gram H_2/min is equivalent to 26.8 A-hr X 60 min/hr X 0.7V X 1/min = 1125 watts, i.e. 1liter H_2/minute can power a 100W fuel cell. Since ~5% of the 0.25 grams of our total catalyst weight was active Ru, Figure 1 illustrates that our H_2 generator produced the equivalent of ~ 0.3kW per gram Ru catalyst at 25°C and ~ 2kW/gram Ru catalyst at 55°C! Greater H_2 generation rates (and power levels) are expected for higher Ru loadings.

Prototypes of our H_2 generator have been used to power a commercial 35 watt H_2/air PEM fuel cell. For applications requiring long-term operation, H_2/air PEM fuel cells together with a NaBH$_4$ H_2 generator is considerably more advantageous than using rechargeable batteries. Our NaBH$_4$ generator can be quickly refueled by simply filling the reservoir with fresh NaBH$_4$ solution (the Ru catalyst is reusable).

Conclusions

Stabilized NaBH$_4$ solutions are an effective source for producing H_2. Due to system simplicity (NaBH$_4$ solution simply contacts Ru to produce H_2), it can be used for numerous applications where H_2 gas is used e.g. PEM fuel cells. High H_2 generation rates have been achieved from NaBH$_4$ solutions with tiny amounts of Ru supported on anion exchange resins. Optimizing catalyst loading, supports, and [NaBH$_4$], will lead to greater H_2 generation rates.

Acknowledgements

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Table 1. Comparison between generating H_2 by chemical hydrides and by aqueous borohydride solutions.

| PARAMETERS	CONVENTIONAL CHEMICAL HYDRIDE	BOROHYDRIDE
System	Water dripping on solid hydride	Borohydride solution contacting catalyst
Theoretical H_2 Storage	<10%	10.8%
H_2 contaminants	Possibly CO and CO_2 (from binders) Possibly SO_2 or NO (from acids)	None expected
Heat generated	Excessive	Moderate
Components carried	Water and dry hydride	Borohydride solution and catalyst
What limits H_2 generation rate?	Rate at which water drips on solid hydride	Surface area of catalyst
What determines total H_2 produced?	Amount of solid hydride	Amount of borohydride solution
H_2 source	Water +Solid	Solution + Catalyst
Is reactant moisture sensitive?	Yes	No
Technical roadblocks	Solids tend to cake. Binders are needed to hold solids together	?
If too much liquid enters cell	Violent reaction	Reaction rate is limited by catalyst surface area.

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Table 2. Rate of H₂ generated catalytically per gram of catalyst (Ru + support resin) for various anionic and cationic support resins in 20% NaBH₄,.10% NaOH, 70% H₂O solution at 25°C. All catalysts had ~5% Ru loading.

Ru Resin Support	Time to generate 1 liter H₂ gas (seconds)	Weight of Ru + support (grams)	Liters H₂/sec. per gram catalyst X 10⁵
ANIONIC RESINS			
A-26	1161	0.2563	336
A-26	633	0.5039	313
IRA-400	1173	0.2565	332
IRA-400	773	0.4116	314
IRA-900	1983	0.2555	197
Dowex 550A	672	0.7692	193
Dowex MSA-1	791	0.7691	164
Dowex MSA-2	1028	0.7691	126
A-36	1415	0.2550	111
CATIONIC RESINS			
MSC-1B	2351	0.2592	164
Dowex HCR-W2	895	0.7631	146
MSC-1A	1382	0.5054	143
Amberlyst 15	2871	0.2563	136
Amberlyst 15	1324	0.5054	149
Dowex 22	1818	0.7678	72
Dowex 88	6163	0.2556	63

Figure 1. Volume of H₂ generated as a function of time by 5% Ru supported on IRA 400 anion exchange resin in 20% NaBH₄,.10% NaOH, 70% H₂O solution at various temperatures.
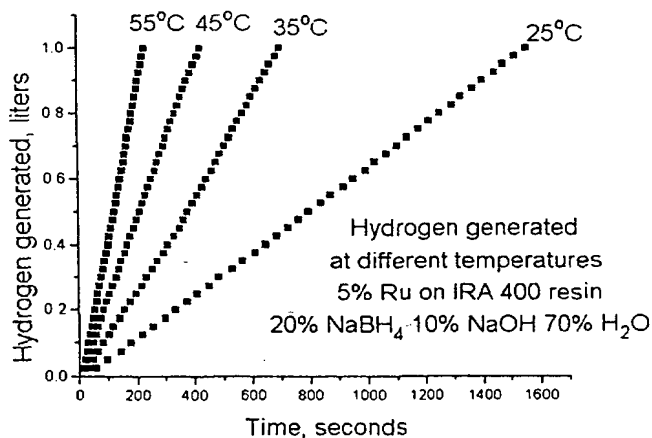
Letter to the Editor

In the October 2000 issue of this journal, Amendola et al. [1] described a hydrogen storage system on board automobiles based on tetrahydroborate.

Its aqueous, but strongly alkaline, solution releases hydrogen only under the presence of a catalyst (e.g. Ru) according to

$$NaBH_4 \cdot 2H_2O \xrightarrow{Catalyst} 4H_2 \cdot NaBO_2 \cdot Heat \ (300 \, kJ). \tag{1}$$
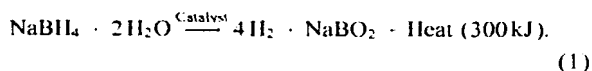
Thus, the liquid and nonflammable $NaBH_4$-solution could directly be delivered at gasoline stations under ambient conditions. Together with the relatively high storage capacity of up to 7% hydrogen by weight, all these properties seem to be advantageous.

Since I have thought about a similar system based on MgH_2 [2], I would like to ask the authors to answer the following two questions:

1. The reconversion of sodium borate ($NaBO_2$) into $NaBH_4$ is energy intensive. Can the authors quantify this question by an efficiency consideration, e.g. in the form: electrical and thermal input energy relative to the LHV of the effectively released amount of H_2?

2. Obviously, all the water in the equation has to be on board from the very beginning. Is it possible in your system to get the water on board? Is it possible, e.g. by condensing the steam in the exhaust — as I have proposed in my system, to reduce the initial weight of the tank but here under the additional condition that the nonflammability of the fuel is not lost?

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References

[1] Amendola SC et al. A safe, portable, hydrogen gas generator using aqueous borohydride solution and Ru catalyst. Int J Hydrogen Energy 2000;25: 969–75.
[2] Seifritz W. Partial and total reduction of CO_2-emissions of automobiles using CO_2-Traps. Int J Hydrogen Energy 1993;18(3):243–51.